

NEW DIMETHYLGLYOXIME PSEUDOHALIDE COMPLEXES

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ABSTRACT

In this study, Three new metal pseudohalide complexes, $[\text{Co}(\text{dmg})_2(\text{N}_3)_2]$ (1), $[\text{Cu}(\text{dmg})(\text{Lys})(\text{N}_3)_2]$ (2) $[\text{Ni}(\text{dmg})_2(\text{N}_3)_2]$ (3) have been synthesized from dimethylglyoxime and lysine. The structures of these metal complexes were proposed based upon IR spectroscopy. These mixed pseudohalide complexes are showing trans-coordination with short bridging ligand(N_3). Three complexes were reported in this paper and proposed their chemical structures with the help of chem draw. These structures are in good agreement with IR frequencies.

KEYWORDS: Dimethylglyoxime (DMG), Coordination Chemistry, Cu(II), Co(II), Complex, Ni(II), Aminoacid

INTRODUCTION

In general, oxime and dioxime derivatives are very important compounds in the chemical industry and in medicine. Copper(II)-containing vicdioximes currently are used as cerebral and myocardial perfusion imaging agents¹. Recently, B.Kishore Babu. Et al published Fe(II), Cd(II) and Pb(II) dimethylglyoxime pseudohalide complexes in the International journal². Recent studies focused on the transition-metal complexes of aminoacids and its isomers. structural, thermodynamic, spectral, and kinetic methods have been widely applied to characterize their physicochemical properties³⁻⁹. In general, aminoacids bond to metal centers by the amino N atom, carboxylate O atoms, and phenolate O atom. The carboxylate groups can coordinate to a metal ion in a monodentate⁵, chelate⁶ or bridging fashion, depending on their physicochemical properties³⁻⁹. Amino acid complexes are used in conventional livestock production to protect trace minerals during digestion^{10, 11}. The metal lysine complexes of this invention are formed with iron, copper, zinc, manganese, and cobalt, all of which play important roles in metabolic processes. Metal complexes have been synthesized, extending our previous work and the objective was to add new complexes to the literature of coordination chemistry.

EXPERIMENTAL

Reagents

All chemicals were purchased from Ranbaxy chemicals and used without further purification.

SYNTHESIS

Synthesis of $[\text{Co}(\text{dmg})_2(\text{N}_3)_2]$ (1)

An aqueous (5 ml) solution of Cobalt nitrate (0.291g, 1.0 mmol) was added to an methanolic solution (5ml) of dmg (0.232g, 2.0 mmol) under stirring conditions and the solution turned to wine red colour and then aqueous solution of sodium azide (0.065g, 1.0 mmol) was added which turned to dark red solution and on addition of tyrosine (tyr) (0.181g, 1.0 mmol) dissolved in 10 ml of sodium hydroxide solution resulted into reddish brown solution. After constant stirring at room temperature for 30 minutes, The solution was filtered off, brown precipitate was formed and the light brown colour solution was left for slow evaporation in the beaker and black crystals were obtained in 3 days. The expected

complex is $[\text{Co}(\text{dmg})(\text{tyr})(\text{N}_3)_2]$, But the obtained complex is $[\text{Co}(\text{dmg})_2(\text{N}_3)_2]$. The absence of peaks in the range of $1578\text{--}1593\text{ cm}^{-1}$ confirms the non coordination of amino acid.

Molecular Formula: $\text{C}_8\text{H}_{16}\text{CoN}_{10}\text{O}_4$; Mol. Wt.: 375.21

IR Data: 3350, 2964, 2037, 1442, 1143, 1087, 740, 513.

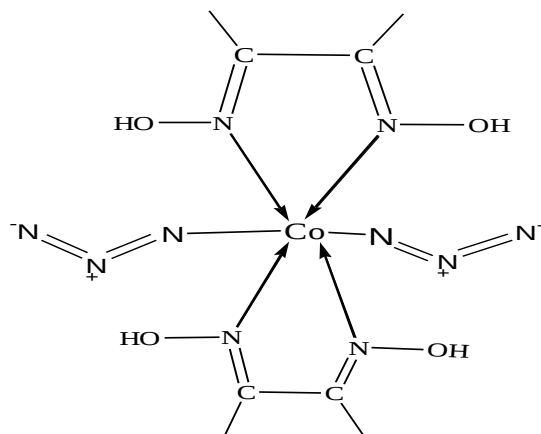


Figure 1: Proposed Structure of $[\text{Co}(\text{dmg})_2(\text{N}_3)_2]$

Synthesis of $[\text{Cu}(\text{dmg})(\text{Lys})(\text{N}_3)_2]$ (2)

An aqueous (5 ml) solution of Lysine (0.164g, 1.0 mmol) was added to a methanolic solution (5ml) of dmg (0.232g, 2.0 mmol) under stirring conditions and the solution remained colourless and then aqueous solution of sodium azide (0.065g, 1.0 mmol) was added which remained as same solution and on stirring white precipitate formed and on addition of aqueous solution of copper acetate (0.199g, 1.0 mmol), thick brown solution formed. After constant stirring at room temperature for 30 minutes, The brown solution was filtered off, brown precipitate was formed and the light brown colour solution is left for slow evaporation in the beaker and brown crystalline precipitate was formed on the next day.

Molecular Formula: $\text{C}_{10}\text{H}_{20}\text{CuN}_{10}\text{O}_4$; Mol. Wt.: 407.88

IR Data: 3414, 3074, 2856, 2075, 1599, 1471, 1157, 1024, 758, 412.

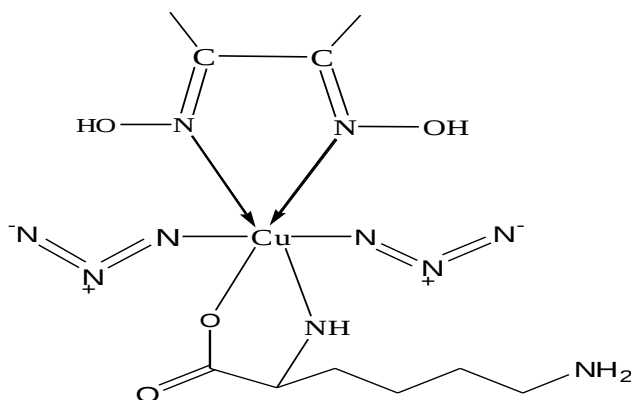


Figure 2: Proposed Structure of $[\text{Cu}(\text{dmg})(\text{Lys})(\text{N}_3)_2]$

Synthesis of $[\text{Ni}(\text{dmg})_2(\text{N}_3)_2]$ (3)

A methanolic (5 ml) solution of 1,10 phenanthroline (0.198g, 1.0 mmol) was added to an aqueous solution (5ml) of Nickel chloride (0.237g, 1.0 mmol) under stirring conditions and the solution turned violet, but on the addition of dmg

(0.116g, 1.0 mmol) Orange red precipitate was formed. Then aqueous solution of sodium azide (0.065g, 1.0 mmol) was added which remained as same solution. After constant stirring at room temperature for 30 minutes, The solution was filtered off, Orange red precipitate was formed and the colourless solution is left for slow evaporation in the beaker and brown crystals were formed within 4 days. The expected complex is $[\text{Ni}(\text{dmg})(\text{Phen})(\text{N}_3)_2]$. But the obtained complex is $[\text{Ni}(\text{dmg})_2(\text{N}_3)_2]$. In this preparation the 1,10 phenanthroline did not coordinate to the metal, this was confirmed by the absence of peaks at 1520 and 1427 in IR spectrum.

Molecular Formula: $\text{C}_8\text{H}_{16}\text{N}_{10}\text{NiO}_4$; Mol. Wt: 374.97

IR Data: 3375, 2031, 1585, 1421, 1138, 1091, 736.

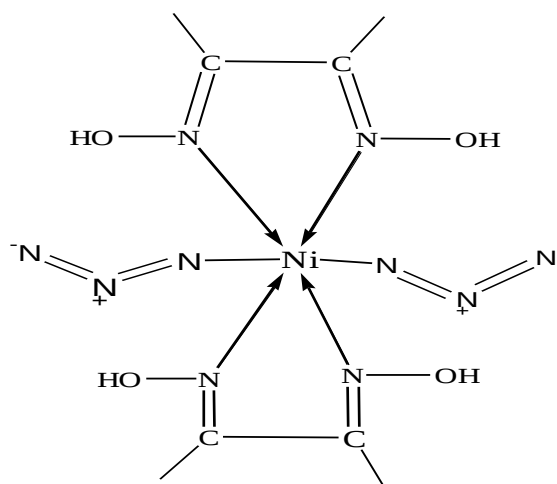


Figure 3: Proposed Structure of $[\text{Ni}(\text{dmg})_2(\text{N}_3)_2]$

RESULTS AND DISCUSSIONS

Physical Properties

Table 1: Color, Yield, Melting Point and Solubility Data for the Complexes

COMPOUND	COLOR	YIELD	M.P.	SOLUBILITY
L	White	-	240 ⁰ C	Methanol
$[\text{Co}(\text{L})_2(\text{N}_3)_2]$	Black	51.5%	Above 300 ⁰ C	Methanol
$[\text{Cu}(\text{L})(\text{Lys})(\text{N}_3)_2]$	Brown	61.8%	Above 300 ⁰ C	Methanol
$[\text{Ni}(\text{L})_2(\text{N}_3)_2]$	Brown	70.8%	Above 300 ⁰ C	Methanol

L = Dimethyl glyoxime(dmg)

Lys = Lysine

N_3 = Azide

IR SPECTRA

The assignment of some of the most characteristic FT-IR band of the complexes are shown in Table (2) together with that of dmg recorded for comparative purposes and facilitate the spectral analysis. Absorption bands in the 2050-2070 cm^{-1} region are considered to be due to metal-nitrogen(of pseudohalide) vibrations^{12,13} while those occurring around 1143 cm^{-1} are thought to arise from nitrogen-oxygen vibration in coordinated dmg^{14,15}. $\nu(\text{C}=\text{N})$ band appearing at 1447 cm^{-1} in dimethylglyoxime is slightly shifted to 1444 cm^{-1} , This suggests that dmg is coordinated to the metal ion through the nitrogen atom of oxime. In the IR spectra of the complex 1 there is a strong and sharp absorption around 513 cm^{-1} which is assigned to the $\nu(\text{Co}-\text{N})$ vibration, these bands are not found in the spectrum of the ligand. The sharp and weak band

occurring around 1020 cm^{-1} and 1145 cm^{-1} in all the complexes is assigned to the N - O stretching vibration of the oxime moieties¹⁶. The spectra of aminoacids exhibit $\nu(\text{NH}_3^+)$ bands in the $3030\text{--}3130\text{ cm}^{-1}$ range. In the complexes, the $\nu(\text{NH}_3^+)$ band is shifted to higher wavenumbers. The peak at 3074 in complex 2 confirms the complexation of aminoacid¹⁶. The bands of medium intensity appearing at $1578\text{--}1593\text{ cm}^{-1}$ are due to the asymmetric stretching vibration of the COO moiety^{17,18}.

Table 2: Selected Characteristics IR Bands ($4000 - 400\text{ CM}^{-1}$)

Complex	$\nu(\text{OH})$	$\nu(\text{NH})_y$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{O})$	$\nu(\text{C}=\text{N}-\text{O})$	$\nu(\text{M}-\text{N}_x)$	$\nu(\text{COO})_y$	
							asym	sym
dmg	3400	-	1570	1141	756	-	-	-
1	3350	-	1442	1143	740	2037	-	-
2	3414	3074	1450	1157	758	2075	1599	1471
3	3375	-	1421	1138	736	2031	-	-

Complex 1 = $[\text{Co}(\text{L})_2(\text{N}_3)_2]$

Complex 2 = $[\text{Cu}(\text{L})(\text{Lys})(\text{N}_3)_2]$

Complex 3 = $[\text{Ni}(\text{L})_2(\text{N}_3)_2]$

L = Dimethyl glyoxime; Lys = Lysine; N_3 = Azide

X = Pseudohalide

Y = Aminoacid

CONCLUSIONS

Our research group presented the results of the synthesis and characterization studies of a series of mixed-ligand complexes involving dimethylglyoxime, Lysine and pseudohalide short bridging ligands. The IR spectra reveals the existence of functional groups and coordinated pseudohalide ions, confirms the complexation of metal and ligand.

ACKNOWLEDGEMENTS

BKB acknowledges grants from the Ref No: 42-354/2013 UGC (INDIA), New Delhi. We are grateful for the technical assistance provided by the Department of Engineering Chemistry at the andhra University, visakhapatnam (INDIA) and the University of Hyderabad for providing the spectral data.

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